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Polyelectrolyte Gels Comprising a Lipophilic, Cost-Effective Aluminate as Fluorine-Free Absorbents for Chlorinated Hydrocarbons and Diesel Fuel

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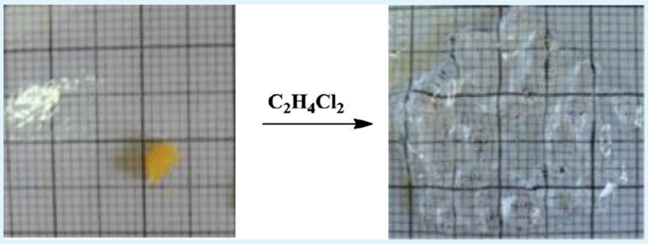
Supporting Information



ABSTRACT: Superabsorbent polymers comprising a lipophilic, halogen-free, and cost-effective aluminate ("altebate") anion have been synthesized. The polyelectrolytes are based on octadecyl acrylate monomers, 0.8−1 mol % ethylene dimethacrylate cross-linker, and 5 mol % N-3-acroyloxypropyl trialkylammonium altebate. At 30 °C, swelling degrees of 70 (chlorobenzene), 102 ($CHCl_3$), 130 (THF), 163 ($ClCH_2CH_2Cl$), 171 (dichlorobenzene), and 208 (CH_2Cl_2) have been determined. The polyelectrolyte absorbs reversibly diesel fuel with a swelling degree of 34, even in the presence of water. Swelling times and critical swelling temperatures have also been determined. The challenges for the development of oil absorbents are discussed.

KEYWORDS: *electrolyte gel, critical temperature, diesel fuel, fluorine-free, lipophilicity, oil absorbent, superabsorbent polymer, swelling*

INTRODUCTION

Superabsorbent polymers for water are widely established, in particular cross-linked sodium polyacrylate in diapers, personal hygiene products, and soil additives.[1] The osmotic pressure of the polyelectrolyte relative to water is a mandatory thermodynamic driving force.[2,3] Cross-linking density and particle size define mechanic properties and equilibrium swelling ratio of the polymer.[3] In 2007, the first superabsorbent polymers for less polar solvents were presented by the group of Sada.[4,5] A cross-linked octadecyl acrylate polymer with ammonio substituted acrylate ester salts was electrostatically neutralized with $BArF_{24}$ anions (Figure 1, left structure).[6] There, the active principle of superarbsorbents for water with its hydrophilic sodium carboxylate fragments has been transferred to a polymer with lipophilic alkyl substituents, quarternary ammonium fragments, and hydrophobic borate counterions. A major challenge for lipophilic polyelectrolytes is presumably the separation of its contact ion pairs by nonpolar solvent. Thereby, the concentration of solutes is increased, and the organic solvent in the absorbent becomes hypertonic. The aim of our work is to synthesize and characterize a new, even more lipophilic building block for oil absorptive polymers.[7]

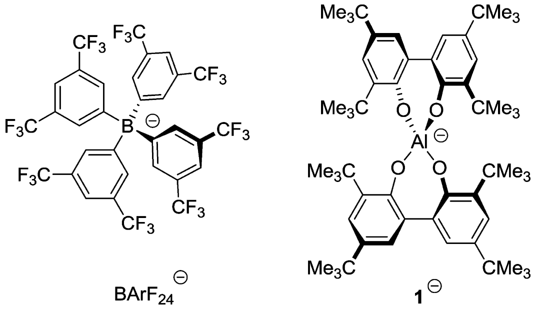


Figure 1. Structure of $BArF_{24}$ and of the cost-effective, halogen-free, lipophilic "altebate" anion 1^-.

Our group synthesized salts of a highly lipophilic aluminate anion. The lithium salt of this "altebate" anion $\mathbf{1}^-$ (Figure 1, right structure) is exceptionally soluble (7 g/L) in pentane at room temperature.[8] Because of its advantages such as low cost of starting materials, and the lack of persistent C−F bonds, we incorporated this aluminate anion in superabsorbent electrolyte gel.

The exchange of expensive fluorinated anions by the highly lipophilic altebate promised both better cost perspectives for applications and a superior aptitude for the absorption of nonpolar solvents and liquid hydrocarbon fuels. While large-scale solvent spills are a rather rare phenomenon, fuel leakages are unfortunately more common. Such incidents require effective means to contain the pollution. Another application for superabsorbent polymers is to absorb volatile organic compounds as proposed by Ohta et al.[9]

RESULTS AND DISCUSSION

Syntheses of Lipophilic Monomers. A synthetic protocol to incorporate the altebate anion into different ammonio substituted acrylate ester salts has been established (Scheme 1). All lipophilic altebate salts (**4a−4d**) were synthesized in a three

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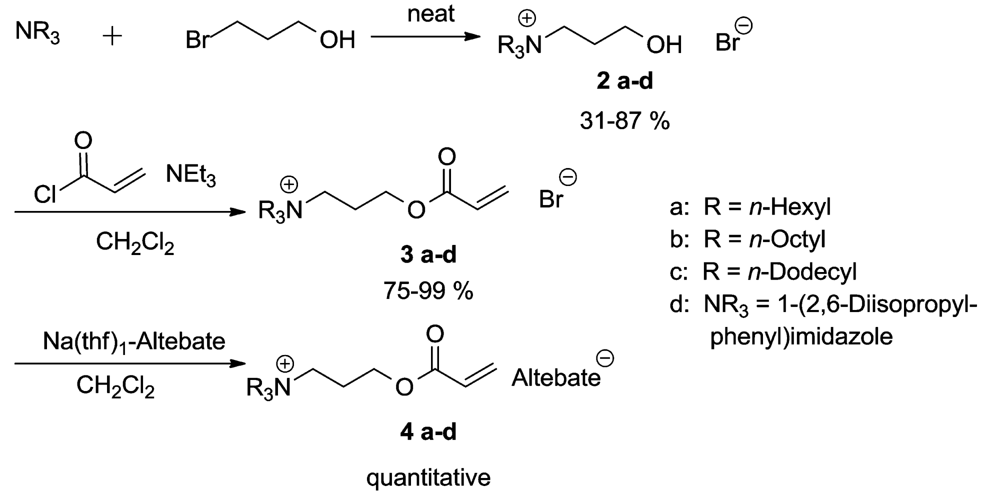
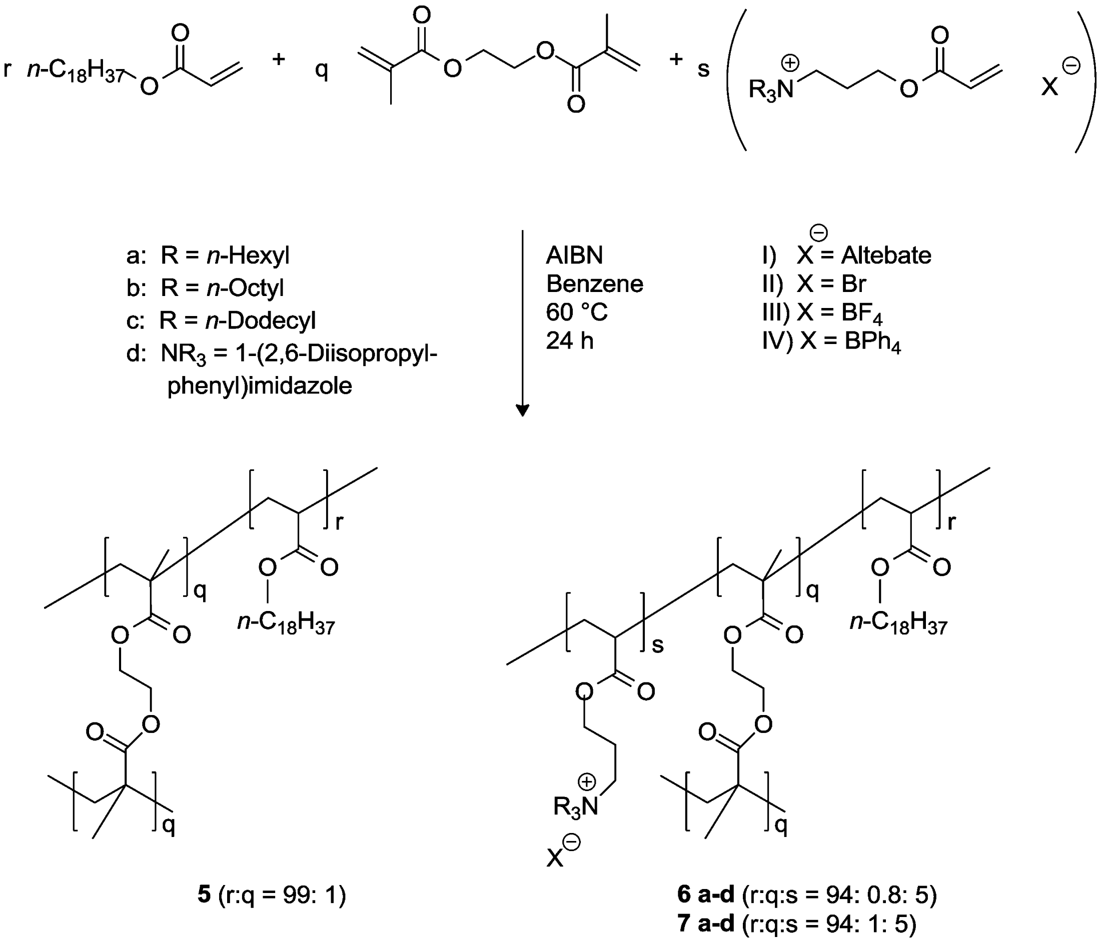
Scheme 1. Preparation of Lipophilic Acrylate Ester Salts



Scheme 2. Syntheses of Nonionic Gels and Electrolyte Gels



step syntheses with good yields in a multiple gram scale. The syntheses of compounds **2b**−**2c** and **3b**−**3c** have been reported in the patent literature without spectroscopic characterization.[10] The synthesis of imidazolium salt **2d** has been published.[11]

The polymerization reactions to the electrolyte gels succeeded in standard NMR tubes. Upscaling, however, proved to be challenging. The tetrafluoroborate, tetraphenylborate, and bromide salts of acrylate esters (Scheme 2, X = II, III, IV) are insoluble in benzene, but soluble in 1,2-dichloroethane. However, for all three salts, ionic monomers were not incorporated into the polymer. Swelling degrees and appearance of the resulting polymers resembled those of nonionic gels. Thus, the copolymerization of the monomer mixture relies on the high lipophilicity of the anions. Ono et al. incorporated dodecyl sulfate and an imidazolato bis(triarylborate) into electrolyte gels.[12] However, fluorinated anions have so far been compulsory for polymers with high swelling degrees.

Influence of Substituents. The structure of the cationic fragment correlates with the maximum swelling degree of the polymers (Scheme 2). Although n-hexyl and n-octyl substituents at the quaternary ammonia salt result in similar swelling degrees, the use of n-dodecyl side chains leads to a significant decrease in maximum swelling degrees. Imidazolium fragments in the polycationic polymer chain result in moderate swelling degrees (Table 1). Our working hypothesis links long alkyl chains and rigid imidazolium moieties to more stable, ordered domains in the polymer: Thermodynamically stable regions of parallel alkyl chains would disfavor the molecular enclosure of solvent.

Table 1. Swelling Degrees of Polycations Polymerized with a Monomer Concentration of 2 mol/L and 0.8% bis(methacrylate) Crosslinker

polymer	NR_3	Q (25 °C) for THF	Q (25 °C) for CH_2Cl_2
$\mathbf{6a}_{2.00}$	$N(C_6H_{13})_3$	94	141
$\mathbf{6b}_{2.00}$	$N(C_8H_{17})_3$	84	143
$\mathbf{6c}_{2.00}$	$N(C_{12}H_{25})_3$	45	75
$\mathbf{6d}_{2.00}$	2,6-diisopropylphenylimidazole	56	89

Monomer Concentration and Polymer Properties. The maximum swelling degree of the electrolyte gels strongly depends on the concentration of the monomers during the polymerization (Table 2). The best swelling degrees were achieved for electrolyte gels prepared with a low monomer concentration of 1.82 mol/L. Thus, a high solvent ratio appears to result in a polymer structure that is more prone to swelling. The AIBN concentration was varied from 0.035 to 0.100 mol/L, no significant effects on the swelling behavior were observed.

Table 2. Swelling with Respect to Acrylate Monomer Concentrations during the Copolymerization with 0.8% Crosslinker in Benzene

acrylate monomer concentration (mol/L)	polymer	resulting Q for THF	resulting Q for DCM
2.50	$\mathbf{6a}_{2.50}$	29	42
2.22	$\mathbf{6a}_{2.22}$	56	91
2.00	$\mathbf{6a}_{2.00}$	84	143
1.82	$\mathbf{6a}_{1.82}$	114	164

Diesel Fuel. The lipophilic polyelectrolyte gels absorb commercial diesel fuel up to a factor of 34 times the mass of the polymer at 30 °C (Figure 2). To the best of our knowledge, this is the most efficient example of a fuel absorbent polyelectrolyte gel.

At 30 °C, the nonionic gel $\mathbf{5}_{1.82}$ does not absorb diesel fuel. The electrolyte gel $\mathbf{7a}_{1.82}$ absorbs diesel even from biphasic systems of diesel fuel and water, aqueous $NaHCO_3$, or aqueous NaCl with essentially the same factors $Q = 32-34$ (Table 3). Apparently, both the cationic polymer and the comprised aluminate anion $\mathbf{1}^-$ are stable under these conditions.

Critical Swelling Temperatures. The swelling degrees of the polymers strongly depend on the temperature. Below a critical temperature, no swelling is observed, and swollen polymers desorb solvent. This temperature varies with polymer structure and choice of the solvent (Table 4) Iseda et al. found a high swelling ability of polystyrene-based polyelectrolyte gels at low temperature, but they only observed swelling by solvents with a dielectric constant higher than 7.5.[13]

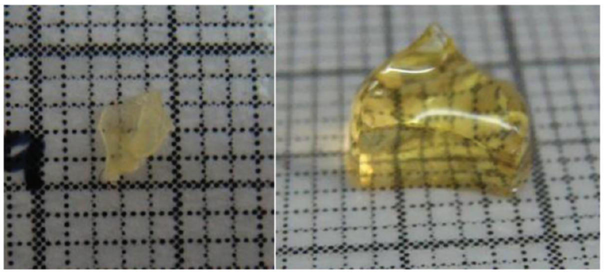


Figure 2. Picture of electrolyte gel $\mathbf{7a}_{1.82}$ before swelling (left) and after swelling (right) in diesel fuel with a swelling degree Q = 34.

Table 3. Swelling Degrees in Biphasic Systems at 30 °C

solvent	$\mathbf{5}_{1.82}$	$\mathbf{7a}_{1.82}$
diesel fuel	0	34
diesel/water	1	33
diesel/aqueous $NaHCO_3$	1	34
diesel/aqueous NaCl	1	32

Table 4. Critical Minimum Swelling Temperature (± 5 °C)

	Critical Minimum Swelling Temperature (°C)	
solvent	$\mathbf{5}_{1.82}$	$\mathbf{7b}_{1.82}$
n-Pentane	25	25
n-Hexane	25	25
n-Heptane	30	25
n-Octane	30	25
n-Nonane	30	25
n-Decane	30	25
n-Dodecane	30	25
n-Tetradecane	40	40
n-Heptadecane	40	40
Diesel fuel	40	40

For cleaning up fuel spills in nontropical areas, lower critical temperatures of the superabsorbent polymers are mandatory. In the case of a phase transition of a polymer domain as origin for the occurrence of critical swelling temperatures, derivatization of the polyelectrolyte backbone would be the logical strategy. Eventually, the UV stability and the mechanical rigidity have to be optimized for some applications.

Swelling Rates.[14,15] The swelling degrees of the electrolyte gel were determined after two day of swelling. The rate of swelling depends on the solvent (Figure 3). After 1 h, the polymer $\mathbf{6a}_{1.82}$ reaches 39% of the maximum swelling degree in dichloromethane, but only 12% in diesel fuel. Electrolyte gel foams feature a faster swelling process. With Diesel fuel, the polymer reaches 70% in 1 h. After 48 h, no further increase in the swelling degrees can be observed.

Absorbing and Nonabsorbing Solvents. The group of Sada reported a notable lack of swelling for ethyl acetate. For their polymer systems, EtOAc is absorbed neither by nonionic gels nor by electrolyte gels.[5,12,13] This behavior is reproduced for our systems (Table 5). Interestingly, solvents such as 1,2-dibromoethane and bromoform with $\varepsilon \approx 5$ are poorly absorbed. This suggests a polarity effect for the absorption of solvents. Even at their boiling points, these liquids were not absorbed. The polyelectrolyte character of the polymer proved to be essential for a high swelling degree in the case of 1,2-

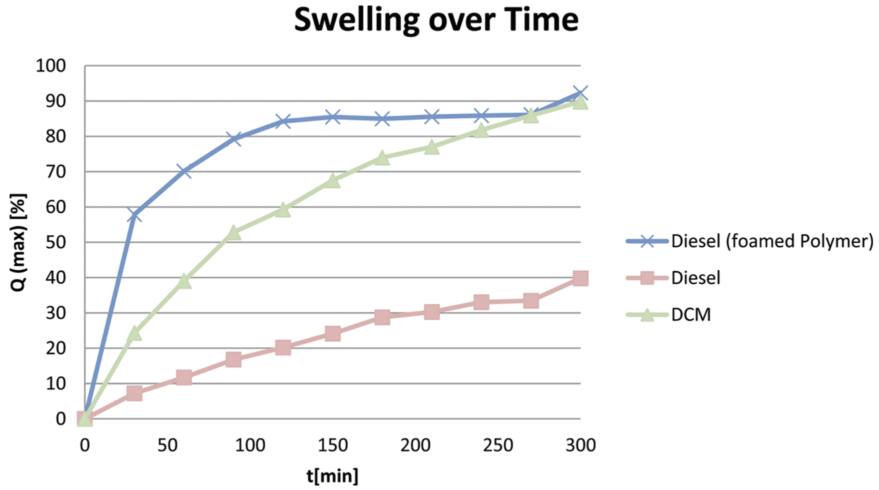


Figure 3. Swelling rate of **$6a_{1.82}$**.

Table 5. Swelling Degrees of the Investigated Polymers at 30 °C after Swelling For 48 h in Various Solvents (values for dielectric constants ε at room temperature)

solvent	ε	Q of $5_{1.82}$	Q of $7a_{1.82}$
water	78.5	0	0
propylene carbonate	64	0	0
acetone	21.5	0	0
THF	7.6	24	130
1,2-dichloroethane	10.4	2	163
1,2-dichlorobenzene	9.9	40	171
dichloromethane	8.9	19	208
chlorobenzene	5.6	35	70
chloroform	4.7	47	102
bromobenzene	5.4	28	62
ethyl acetate	6.0	0	1
1,2-dibromoethane	4.8	3	3
bromoform	4.4	7	9
1,2,4-trichlorobenzene	3.9	43	59
toluene	2.4	26	37
carbon tetrachloride	2.2	35	42
diesel fuel	2.1	0	34
diesel fuel/water		1	33
diesel/aqueous $NaHCO_3$		1	34
diesel fuel/aqueous NaCl		1	32
1-hexene	2	15	16
cyclohexane	2.0	24	24
diethyl ether	4.3	15	21
n-pentane	1.8	13	13

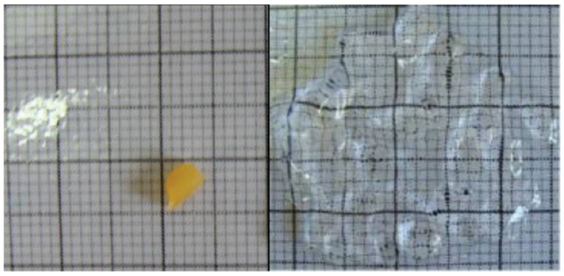


Figure 4. Picture of polyelectrolyte **$7a_{1.82}$** before swelling (left) and after swelling (right) in 1,2-dichloroethane with a swelling degree Q = 163.

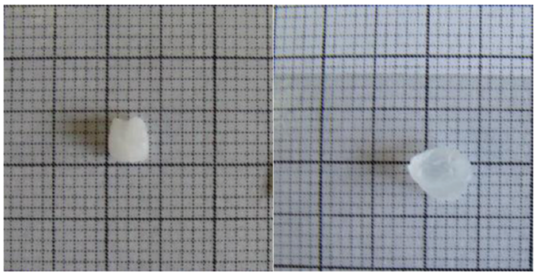


Figure 5. Picture of nonelectrolyte **$5_{1.82}$** before swelling (left) and after swelling (right) in 1,2-dichloroethane with a swelling degree Q = 2.

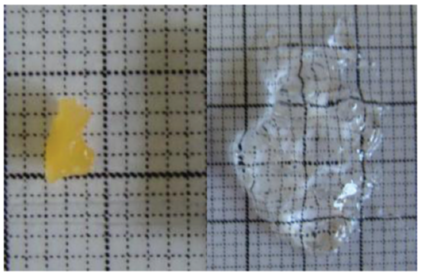


Figure 6. Picture of a polyelectrolyte before swelling (left) and after swelling (right) in THF with a swelling degree Q = 130.

dichloroethane (Figures 4 and 5). THF is the non-chlorinated solvent with the highest swelling degree (Figure 6).

Polyelectrolytes with expensive fluorinated counterions of the Sada group feature similar swelling degrees of 99 and 122 in chloroform, 70 and 109 in chlorobenzene, 121 and 119 in tetrahydrofuran, 128 and 224 in dichloromethane, and 157 and 181 in 1,2-dichloroethane.[12]

■ SUMMARY

Electrolyte gels comprising the halogen-free and cost-effective altebate anion have been synthesized. High swelling degrees for chlorinated hydrocarbons and THF stand in contrast to no swelling for acetone, ethyl acetate, or low swelling degrees for bromoalkanes. For hydrocarbons and diesel fuel, swelling degrees of 10 to 40 have been measured. Diesel fuel is also absorbed in the presence of water or brine. A decrease in critical swelling temperatures by, for example, derivatization of the polymer backbone would expand the range and impact of potential applications.

■ EXPERIMENTAL SECTION

Starting materials were used as supplied by Acros Organics, Aldrich Chemical Co. and BASF SE without further purification. Altebate salts were prepared according to literature protocols.[8] Diesel fuel was obtained from Shell Germany ("SaveFuel"). Reactions involving air-sensitive reagents were carried out in an atmosphere of nitrogen or argon using standard Schlenk techniques. Absolute solvents were dried in an MBRAUN MB SCS-800 solvent purification system. NMR spectra were recorded using Bruker ARX-250, Bruker Avance 300 and Bruker Avance 500 spectrometers. Chemical shifts are reported in ppm relative to TMS for ^{1}H and ^{13}C and were determined by reference to the residual ^{1}H or ^{13}C solvent peaks. Melting points were determined using a Gallenkamp hot-stage microscope and are uncorrected.

Measurement of the Swelling Degrees. The vacuum-dried polymer was cut into small pieces (≈ 3 mg). The sample was allowed to swell in 4 mL of solvent at constant temperature. If not otherwise specified, the polymers were swollen for 2 days at 30 °C. Often, significantly less time is sufficient to approach the maximum swelling factor. However, we used a standard time of 48 h to get reliable and comparable values for larger pieces of polymer. The polymer was filtered over a metal sieve and quantified with a special accuracy weighing scale. The swelling factor was determined by the equation

$$Q = \frac{m_{\mathrm{swollen}} - m_{\mathrm{dry}}}{m_{\mathrm{dry}}}$$

Preparation of N-(3-Hydroxypropyl)-N,N,N-trihexylammonium Bromide (2a). Under inert gas conditions, 3-bromopropan-1-ol (1.0 g, 7.19 mmol) and trihexylamine (0.47 g, 1.74 mmol) were heated under reflux conditions for two days. The product was precipitated by addition of 50 mL of diethyl ether. The colorless product was filtered and 0.61 g (1.49 mmol, 87%) of colorless powder was obtained. ^{1}H NMR: ($CDCl_3$; 300.13 MHz) δ_H = 3.98 (s, 1 H), 3.73 (t, 2 H, $^{3}J_{H,H}$ = 4.5 Hz), 3.58 (t, 2 H, $^{3}J_{H,H}$ = 6.0 Hz), 3.21 (t, 6 H, $^{3}J_{H,H}$ = 9.0 Hz), 1.95 (m, 2 H), 1.67 (m, 6 H), 1.32 (m, 18 H), 0.87 (t, 9 H, $^{3}J_{H,H}$ = 6.0 Hz) ppm. ^{13}C-{^{1}H} NMR: ($CDCl_3$; 75.47 MHz) δ_C = 59.26, 57.94, 31.3, 26.2, 25.7, 22.5, 22.2, 13.8 ppm. $C_{21}H_{46}BrNO$ (408.50): calcd. C 61.74, H 11.35, N 3.43; found C 61.66, H 11.54, N 3.37. Mp. 91 °C. IR (KBr): $\tilde{\nu}$ = 3422, 3203, 2955, 2925, 2871, 2855, 1635, 1467, 1414, 1385, 1162, 1145, 1095, 1071, 947, 864, 797, 725, 662, 575 cm^{-1}. MS (HR-ESI+): *m/z* calcd. 328.35794; found 328.35696 $[M]^+$.

Preparation of N-[3-(Acryloyloxy)propyl]-N,N,N-trihexylammonium Bromide (3a). Under inert gas conditions, N-(3-hydroxypropyl)-N,N,N-trihexylammonium bromide (3.94 g, 9.64 mmol) was dissolved in 30 mL of CH_2Cl_2. Four equivalents of triethylamine (5.44 mL, 39.2 mmol) were added under ice cooling. Two equivalents of acryloyl chloride (1.57 mL, 19.4 mmol) were added slowly. The reaction mixture was stirred for 24 h. The excess of acryloyl chloride was quenched with a saturated aqueous $NaHCO_3$ solution, extracted three times with 50 mL CH_2Cl_2 and dried over $MgSO_4$. Removal of the solvent in vacuo gave an orange-brown oil (3.90 g, 8.43 mmol, yield 88%). ^{1}H NMR: ($CDCl_3$; 300.13 MHz) δ_H = 6.42–5.92 (m, 3 H), 5,28 (CH_2Cl_2), 4,33 (t, 2 H, $^{3}J_{H,H}$ = 5.7 Hz), 3.54 (t, 2 H, $^{3}J_{H,H}$ = 8.4 Hz), 3.38 (t, 6 H, $^{3}J_{H,H}$ = 8.4 Hz), 2.23 (m, 2 H), 1.67 (m, 6 H), 1.32 (m, 18 H), 0.87 (t, 9 H, $^{3}J_{H,H}$ = 6.6 Hz) ppm. ^{13}C{^{1}H} NMR: ($CDCl_3$; 75.47 MHz) δ_C = 165.9, 131.9, 127.8, 61.1, 59.4, 56.5, 31.3, 26.1, 22.5, 22.3, 13.8 ppm. $C_{24}H_{48}BrNO_2$ (462.55): calcd C 62.32, H 10.46, N 3.03; found C 63.31, H 10.09, N 2.94. IR (KBr): $\tilde{\nu}$ = 2958, 2930, 2860, 1724, 1636, 1618, 1489, 1467, 1408, 1380, 1339, 1295, 1271, 1192, 1063, 984, 864, 811, 729, 695 cm^{-1}. MS (HR-ESI+): *m/z* calcd 382.36796; found 382.36799 $[M]^+$.

Preparation of N-[3-(Acryloyloxy)propyl]-N,N,N-trihexylammonium Altebate (4a). Under inert gas conditions, sodium altebate (2.0 g, 2.16 mmol) was suspended in 30 mL of CH_2Cl_2 and a solution of N-[3-(acryloyloxy)propyl]-N,N,N-trihexylamonium bromide (1.0 g, 2.16 mmol) in 20 mL of CH_2Cl_2 was added. The reaction mixture was stirred for 30 min and filtered over Celite. After removal of the solvent in vacuo, a yellow foam (3.0 g, quantitative) was obtained. We were not able to separate the product from NaCl. ^{1}H NMR: ($CDCl_3$; 300.13 MHz) δ_H = 7.16 (d, 4 H, $^{4}J_{H,H}$ = 2.7 Hz), 6.95 (d, 4 H, $^{4}J_{H,H}$ = 2.4 Hz), 6.38 – 5.92 (m, 3 H), 5.60 (CH_2Cl_2), 4.28 (t, 2 H, $^{3}J_{H,H}$ = 5.7 Hz), 3.65 (t, 2 H, $^{3}J_{H,H}$ = 8.4 Hz), 3.52 (t, 6 H, $^{3}J_{H,H}$ = 8.4 Hz), 2.30 (m 2 H), 1.89 (m, 6 H), 1.37 (m, 18 H), 1.30 (s,72 H), 0.88 (t, 9 H, $^{3}J_{H,H}$ = 6.9 Hz) ppm. ^{13}C{^{1}H} NMR: ($CDCl_3$; 75.47 MHz) δ_C = 166.3, 157.1, 139.0, 138.6, 133.7, 132.0, 129.2, 128.7, 122.3, 61.9, 59.9, 56.8, 36.1, 34.8, 31.4, 30.9, 22.7, 26.9, 32.2, 31–29 14.4 ppm. Mp. 160 °C. IR: $\tilde{\nu}$ = 3433, 2958, 2871, 1734, 1635, 1465, 1432, 1405, 1387, 1360, 1282, 1241, 1200, 1172, 1131, 1099, 874, 783, 769, 607 cm^{-1}. MS (HR-ESI): *m/z* calcd. 382.36796; found 382.36791 $[M]^+$, calcd. 843.58775; found 843.58566 $[M]^-$.

Typical Preparation of Gels. A standard NMR tube is charged with octadecyl acrylate (650 mg, 2.0 mmol), ethylene dimethacrylate (3.5 μL, 22 μmol), N-[3-(acryloyloxy)propyl]-N,N,N-trihexylammonium altebate (140 mg, 0.1 mmol), AIBN (5 mg) and 0.4 mL of benzene. The solution was polymerized by heating at 60 °C for 24 h. After polymerization, the NMR tube was destroyed and the crude polymer was obtained as a yellow soft material. This polymer was washed by swelling in benzene for 24 h and further filtration of the solution. The polymer was dried in air for 2 days followed by 6 h drying in vacuo (1 × 10^{-2} mbar).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional synthetic protocols and figures of NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

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Notes

The authors declare the following competing financial interest(s):The University of Heidelberg and the Technologie-Lizenzburo Karlsruhe TLB have filed a patent application on the synthesis and the application of altebate salts.

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■ DEDICATION

This manuscript is dedicated to Prof. Dr. Herbert Mayr on the occasion of his 65th birthday.

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